CLAIMS:

1. A controlled polymerization process, comprising:

polymerizing free radically (co)polymerizable monomers in the presence of a system initially comprising:

an initiator having a radically transferable atom or group; and

a catalyst which participates in a reversible cycle with at least one of the initiator and a compound having a radically transferable atom or group; and

forming a (co)polymer.

2. The process of claim 1, wherein the initiator contains a second functional group.

3. The process of claim 2, wherein the second functional group comprises a polar substituent.

4. The process of claim 3, wherein the polar substituent is a carboxylic acid group.

5. The process of claim 1, wherein the free radically (co)polymerizable monomers are chosen from a group consisting acrylates, (meth)acrylates and (meth)acrylamides.

6. The process of claim 1, further comprising:

preparing the initiator having a radically transferable atom or group by decomposing a first standard free radical initiator to a radical in the presence of a transition metal salt in a higher oxidation state, the transition metal salt comprising:

a radically transferable counterion, wherein the transition metal salt transfers the radically transferable counterion to the radical of the first initiator to form the initiator and the transition metal salt in a lower oxidation state.

7. The process of claim 6, wherein the catalyst is the transition metal salt in the lower oxidation state.

8. The process of claim 7, wherein the transition metal comprises a complex counterion.

9. The process of claim 8, wherein the complex counterion is an onium based counterion.

10. The process of claim 1, wherein the catalyst comprises a transition metal salt.

11. The process of claim 10, wherein the transition metal salt is based on at least one of a group consisting of iron, copper, nickel, manganese and chromium.

12. The process of claim 10, wherein the counterion is an organic or inorganic counterion.

13. The process of claim 10, wherein the transition metal salt comprises a complex counterion.

14. The process of claim 10, wherein the catalyst is readily removed from the (co)polymer by washing with a solvent.

15. The process of claim 14, wherein the solvent is a polar solvent.

16. The process of claim 15, wherein the polar solvent is water.

17. The process of claim 13, wherein the complex counterion is an onium based counterion.

18. The process of claim 17, wherein the onium based counterion is a charged species comprising at least one atom chosen from a group consisting of N, P, or As.

19. The process of claim 18, wherein the counterion comprises a material chosen from a group consisting of aliphatic amines, phosphines, and arsenes.

20. The process of claim 19, wherein the counterion comprises a material chosen from a group consisting of tetra-alkylammonium, tetra-alkylphosphonium, and tetra-alkylarseonium counterions.

21. The process of claim 13, wherein the transition metal salt comprises a metal based counterion

22. The process of claim 13, wherein the transition metal salt comprises a halide counterion.

23. The process of claim 13, wherein the transition metal salt is arranged in one of a tetrahedral and a square planar configuration with the counterion.

24. The process of claim 13, wherein a molar ratio of the transition metal to the counterion is greater than one.

25. The process of claim 24, wherein the transition metal is iron.

26. The process of claim 1, further comprising:

adding a neutral ligand to increase the rate of reaction.

27. A controlled polymerization process, comprising:

preparing a second initiator having a radically transferable atom or group by decomposing a first standard free radical initiator in the presence of a transition metal salt, the transition metal salt comprising:

a complex counterion; and

a radically transferable atom or group, wherein the transition metal salt transfers the radically transferable atom or group to a decomposition product of the first initiator to form the second initiator;

polymerizing free radically (co)polymerizable monomers in the presence of a system initially comprising:

the second initiator; and

a catalyst which participates in a reversible cycle with at least one of the second initiator and a compound having a radically transferable atom or group.

28. The process of claim 27, wherein the catalyst is the transition metal salt.

29. The process of claim 28, wherein the transition metal salt initially present comprises a transition metal in a higher oxidation state and a transition metal in the metal zero state such that the average oxidation state is lower than that required to react with the molar ratio of initiator.

30. The process of claim 28, wherein the transition metal is iron.

31. The process of claim 27, wherein a polymer is formed having a partial residue of the first initiator at one terminus.

32. The process of claim 31 further comprising:

isolating the polymer.

33. The process of claim 27, wherein the process is performed in one of a bulk system, a system comprising an appropriate solvent, in a suspension, in an emulsion, or over a solid support in a batch, semi-batch or continuous process.

34. The process of claim 27, wherein the complex counterion comprises a charged ligand.

35. A controlled polymerization process, comprising:

preparing an initiator having a radically transferable atom or group by rupturing a peroxide in the presence of a transition metal salt, the transition metal complex comprising:

a radically transferable atom or group, wherein the transition metal complex transfers the radically transferable atom or group to a residue of the peroxide to form the initiator or originator;

polymerizing free radically (co)polymerizable monomers in the presence of a system initially comprising:

the initiator; and

a catalyst which participates in a reversible cycle with the initiator and a compound having a radically transferable atom or group.

36. The process of claim 35, wherein the transition metal complex comprises a transition metal salt.

37. The process of claim 35, wherein the transition metal is copper.

38. The process of claim 35, wherein the transition metal complex comprises a metal in a lower oxidation state.

39. The process of claim 35, wherein a polymer is formed having a partial residue of the peroxide at one terminus.

40. The process of claim 39, further comprising:

isolating the polymer.

41. The process for controlled polymerization of radically (co)polymerizable monomers, comprising the steps:

polymerizing one or more free radically (co)polymerizable monomers in the presence of a system comprising:

an initiator having a first radically transferable atom or group and a carboxylic acid group, and

a transition metal complex capable of undergoing a redox reaction with the initiator or a compound having a radically transferable atom or group, to allow addition of said radically polymerizable (co)monomers to initiator.

42. The process of claim 41, further comprising:

forming a (co)polymer with a terminal carboxylic acid group; and

isolating the (co)polymer.

43. A process for controlled polymerization of radically (co)polymerizable monomers containing free carboxylic acid groups comprising the steps:

polymerizing a first free radically (co)polymerizable monomers and a second free radically (co)polymerizable monomers having a free carboxylic acid group in the presence of:

an initiator containing a radically transferable atom or group; and

a transition metal complex capable of undergoing a redox reaction with the initiator and a compound having a radically transferable atom or group, to allow addition of said radically polymerizable (co)monomers

44. The process of claim 43, further comprising:

forming a (co)polymer with a carboxylic acid group within the polymer chain; and

isolating the (co)polymer.

45. A controlled polymerization process of atom or group transfer polymerization, comprising the steps:

polymerizing one or more radically (co)polymerizable monomers in the presence of a system initially containing;

an initiator having one or more radically transferable atom(s) or group(s),

a transition metal compound comprising one or more counterion(s) attached to a solid support, which interacts with a N-, O-, P-, or S- containing ligand which can coordinate in a σ-bond, or a carbon-containing ligand which can coordinate in a π-bond, to the transition metal; and

wherein the transition metal compound participates in a reversible redox cycle with the initiator or a compound having a radically transferable atom or group.

46. The process of claim 45, further comprising:

preparing the initiator having a radically transferable atom or group by decomposing a first standard free radical initiator to a radical in the presence of the transition metal compound in a higher oxidation state, the transition metal compound comprising:

a radically transferable atom or group, wherein the transition metal compound transfers the radically transferable atom or group to the radical of the first initiator to form the initiator and the transition metal salt in a lower oxidation state.

47. The process of claim 45, wherein the transition metal compound is physically, physicochemically or chemically attached to the surface of the solid support through ionic bonding, physisorption, chemisorption, Van der Waals forces, coordinate or covalent bonding.

48. A controlled polymerization process of atom or group transfer polymerization, comprising the steps:

polymerizing one or more radically (co)polymerizable monomers in the presence of a system initially containing;

an initiator having one or more radically transferable atom(s) or group(s),

a transition metal salt comprising one or more counterion(s) attached to a solid support;

wherein the transition metal catalyst participates in a reversible redox cycle with the initiator or a compound having a radically transferable atom or group.

49. The process of claim 48 wherein the transition metal salt comprises a complex counterion.

50. A controlled polymerization process of atom or group transfer polymerization, comprising the steps:

polymerizing one or more radically polymerizable monomers in the presence of a system initially comprising:

an initiator having one or more radically transferable atom(s) or group(s);

a transition metal salt comprising:

one or more of the counterion(s) attached to a solid support;

a ligand coordinated in a σ-bond to the transition metal,

a redox conjugate of the transition metal compound; wherein at least one of the transition metal and a redox conjugate of the transaction metal salt participate in a reversible redox cycle with at least on of the initiator or a compound having a radically transferable atom or group.

51. The process of claim 50, wherein the redox conjugate of the transition metal is at least partially soluble in the polymerization process.

52. The process of claim 50, wherein the solid support is an ion exchange resin.

53. The process of claim 50, wherein the process is conducted in a batch reactor.

54. The process of claim 50, wherein the process is conducted in a continuous flow system.

55. The process of claim 50, further comprising:

forming the initiator by transferring a radically transferable atom or group from the transition metal salt in a higher oxidation state to a formed free radical.

56. A process for the removal of a transition metal catalyst complex from a polymerization reaction comprising the steps:

contacting a reaction medium to an ion exchange medium wherein the reaction medium comprises:

a polymer;

a catalyst complex.

57. The process of claim 56, wherein the reaction medium further comprises a solvent.

58. The process of claim 57, wherein the solvent has a polarity which enhances the rate of removal of the catalyst complex from the medium.

59. The process of claim 56, wherein the ion exchange resin comprises a crosslink density and a bead size, wherein at least one of the crosslink density and the bead size is chosen to enhance removal of the catalyst complex.

60. The process of claim 56, wherein the catalyst complex is present in the reaction medium comprising at least one of a solution, an emulsion or miniemulsion.

61. The process of claim 60, wherein the emulsion or miniemulsion comprises a suspension medium of an inorganic liquid.

62. The process of claim 60, wherein the emulsion or miniemulsion comprises a suspension medium of water.

63. The process of claim 56, wherein the catalyst complex comprises:

a transition metal in one or more oxidation states;

a ligand; and

a counterion.

64. The process of claim 63, wherein the catalyst complex is bound to the ion exchange medium through a shared counterion on the ion exchange medium.

65. The process of claim 63, wherein the reaction medium is passed over a bed of the ion exchange medium.

66. The process of claim 63, wherein the ligand on the catalyst complex is chosen to allow efficient removal of the transition metal complex from solution by the ion exchange medium.

67. The process of claim 63, wherein the temperature of the reaction media is controlled to modify the rate of removal of transition metal from the reaction media.

68. The process of claim 63, wherein the transition metal is one of either copper or iron.

69. The process of claim 63, further comprising:

separating the ion exchange medium from the reaction medium.

70. The process of claim 69, further comprising:

regenerating the catalyst complex.

71. The process of claim 70, wherein regenerating the catalyst complex comprises:

exposing the ion exchange medium bound transition metal complex to a regeneration medium containing one of an acid or a salt comprising a radically transferable atom or group as a counterion;

separating the regeneration medium from the ion exchange resin.

72. The process of claim 71, wherein the regeneration medium contains free radically (co)polymerizable monomers.

73. The process of claim 71, wherein the equilibrium between the transition metal complex in solution and transition metal complex bound to the ion exchange resin is controlled by adjusting one or more of the temperature of the regeneration medium, polarity of the regeneration medium, ionic character of the ion exchange resin, pH of the regeneration medium, degree of crosslinking of the ion exchange resin or swellability of the ion exchange resin, swellability permeability of the ion exchange resin, acid strength of the supported counterion and gross size of the ion exchange resins.

74. The process of claim 56, wherein the catalyst complex comprises a complex salt.

75. The process of claim 56, wherein the catalyst complex comprises:

a transition metal; and

a complex counterion.

76. The process of claim 75, wherein the ion exchange medium is an ion exchange resin.

77. The process of claim 56, wherein the ion exchange medium has acidic counterions.

78. The process of claim 56, wherein the ion exchange medium comprises cations selected of at least one of H^+ or Na^+.

79. The process of claim 56, wherein the catalyst complex is bound to the ion exchange medium through a shared counterion on the ion exchange medium.

80. The process of claim 56, wherein substantially all of the catalyst complex is removed from the reaction medium.

81. A controlled polymerization process, comprising:

polymerizing free radically (co)polymerizable monomers in the presence of a system comprising:

an initiator having a radically transferable halide;

a transition metal compound; and

a nitrogen containing ligand.

82. The process of claim 81, wherein the free radically (co)polymerizable monomers are (meth)acrylamides.

83. The process of claim 81, wherein the ligand is at least one of a primary or secondary linear amine.

84. The process of claim 83, wherein the ligand is further complexed by a polar solvent to prepare a neutral complex.

85. The process of claim 81, wherein the ligand is a charged species.

86. A process for atom transfer radical addition for adding functionality to an oligomer or polymer, comprising:

reacting a first oligomer or polymer having a radically transferable atom or group with a second compound having a first desired functional group, the second compound reactive with the first oligomer or polymer after removal of the radically transferable atom or group, in the presence of a system initially comprising:

a catalyst which participates in a reversible cycle with the first oligomer or polymer.

87. The process of claim 86, wherein the catalyst comprises a transition metal salt.

88. The process of claim 86, wherein the catalyst comprises a transition metal and further comprising:

adding the transition metal in its metal zero state.

89. The process of claim 86, wherein the second compound is not a free radically polymerizable monomer.

90. The process of claim 89, wherein the second compound comprises a α,α-disubstituted olefin group.

91. The process of claim 86, wherein the catalyst is a transition metal complex.

92. The process of claim 91, wherein the transition metal complex comprising a transition metal and a ligand further comprising adding additional transition metal and, optionally, additional ligand.

93. The process of claim 86, further comprising forming a second oligomer or polymer which is not polymerizable in the system.

94. The process of claim 93, further comprising reacting the second oligomer or polymer with a second compound which is reactive with the second oligomer or polymer, wherein the second compound has a second desired functional group.

95. The process of claim 94, wherein the second compound additionally comprises a fourth desired functional group, the functional groups are thereby incorporated into the polymer at each reactive chain end, wherein the third compound has a structure:

$$CH_2=CR^1-(CH_2)_n-X$$

wherein R^1 is on selected from H, CH_3 or aryl;
n is an integer; and,
X is a functional group.

96. The process of claim 86, wherein the first oligomer or polymer has a plurality of radically transferable atoms or groups.

97. The process of claim 93, wherein the second polymer is one of a homotelechelic-polymer or a heterotelechelic polymer.

98. The process of claim 97, wherein the second desired functional group is subject to further reaction conditions to convert the second functional group into a third functional group.

99. The process of claim 98, wherein the said further reaction forms a double bond.

100. The process of claim 99, wherein the said further reaction includes a dehydrohalogenation reaction.

101. The process of claim 100, wherein the reaction is assisted by the presence of an acid acceptor.

102. The process of claim 86, wherein the second compound is an unsaturated molecule which is not free radically (co)polymerizable and terminates the polymer.

103. The process of claim 102, wherein the unsaturated molecule comprises a second functional group.

104. The process of claim 103, further comprising:

adding a third compound comprising a third functional group, the third compound which reacts with the first functional group incorporated on the polymer.

105. The process of claim 102, wherein the unsaturated molecule is at least one of α, α-disubstituted olefin or an allyl.

106. The process of claim 94, wherein the second desired functional group comprises one of an allyl, epoxy, hydroxy, amino, cyano, carboxy, masked carboxy, alkyl, perhaloalky, silyl, silicon containing moiety or phosphorous containing moiety.

107. A process for a catalytic atom transfer functionalization of oligo/polymeric materials having one or more radically transferable atom(s) or group(s), comprising the steps:

providing a polymer having a radically transferable atom or group; and

adding a compound containing a α,α-disubstituted olefin group to the polymer in the presence of a transition metal complex capable of undergoing a redox reaction with the radically transferable atom or group, resulting in the addition of the compound containing the α,α-disubstituted olefin group at the site of the radically transferable atom or group and an elimination reaction involving the radically transferable atom or group to form a reactive unsaturated group.

108. The process of claim 107, wherein the substituents on the α,α-disubstituted olefin group are individually selected.

109. The process of claim 108, further comprising:

forming a functional polymer having a reactive exo-double bond and wherein one of the substituents is a methyl group.

110. The process of claim 109, further comprising:

forming a functional polymer having an endo-double bond.

111. The process of claim 110, wherein the coupling compound comprises an α-aryl styrene.

112. The process of claim 111, wherein the α-aryl styrene is selected from diphenylethylene, 1,3-bis(1-phenylethenyl)benzene, or 2,2- bis{4-(1-phenylethenyl)phenyl}propane.

113. The process of claim 107, wherein the polymeric material is an oligimer.

114. The process of claim 107, wherein one substituant on the α,α-disubstituted olefin is a methyl group and the formed double bond is predominately a exo-double bond.

115. The process of claim 114, wherein a macromonomer with a reactive exo-double bond is prepared.

116. The process of claim 107, wherein the elimination reaction is enhanced by the addition of an acid acceptor.

117. The process of claim 116, wherein the acid acceptor is selected from the group consisting of basic organic molecules, linear and heterocyclic N containing compounds, ion exchange resins or inorganic acid acceptors.

118. A process for a catalytic atom transfer coupling of polymers comprising:

providing a first polymer having a first radically transferable atom or group;

adding a coupling compound containing one or more α,α-disubstituted olefin group(s) to the first polymer in the presence of a transition metal complex capable of undergoing a redox reaction with the first radically transferable atom or group, resulting in the addition of the coupling compound containing the α,α-disubstituted olefin group at the site of the first radically transferable atom or group and an elimination reaction comprising the radically transferable atom or group to form a reactive double bond; and

allowing a second polymer having a second radically transferable atom or group in the presence of the transition metal complex to add to the reactive double bond.

119. The process of claim 118, wherein the first polymer and the second polymer are substantially similar.

120. The process of claim 119, further comprising:

forming a functional polymer having an endo-bond and wherein the coupling compound comprises an α-alkyl styrene.

121. The process of claim 120, wherein the coupling compound comprises α-methyl styrene.

122. The process of claim 107, further comprising:

forming a functional polymer comprising and enol/ketone and wherein an α-substituent comprises a hydroxyl group.

123. The process of claim 118, wherein the coupling compound is a second polymer comprising an isopropenyl group.

124. The process of claim 123, wherein the α,α-disubstituted olefin group is a pendant functional group of the second polymer.

125. The process of claim 123, wherein the graft copolymer comprise the first copolymer grafted to the second copolymer within the graft copolymer chain..

126. The process of claim 118, the first polymer is a mixture of (co)polymers.

127. The process of claim 118, wherein the second polymer has a similar composition and molecular weight to the first polymer.

128. The process of claim 118, wherein a molar ratio of the total moles of the first polymer and the second polymer to the moles of the coupling compound is controlled to form a third polymer of a configuration of at least one of linear, star, graft, and chain extended materials containing a residue of the first polymer and the second polymer.

129. The process of claim 128, wherein the first polymer includes two transferable atoms or groups and the coupling compound contains two α,α-disubstituted olefin groups allowing the formation of a network copolymer containing multiple units of the first polymer.

130. The process of claim 128, wherein the coupling compound contains one α,α-disubstituted olefin group, the first polymer and second polymer have one radically transferable atom or group and a molar ratio of the total moles of the first polymer and the second polymer to the moles of the coupling compound is essentially 1:0.5.

131. The process of claim 128, wherein the coupling compound contains two α,α-disubstituted olefin groups, the first polymer and second polymer each have one radically transferable atom or group and the molar ratio of the total moles of the first polymer and the second polymer to the moles coupling compound is essentially 1:0.25.

132. The process of claim 131, wherein the first polymer and the second polymer differ in at least one of molecular weight and composition and a star copolymer is formed.

133. The process of claim 132, wherein a hetero-arm star copolymer is formed.

134. The process of claim 131, wherein two α,α-disubstituted olefin groups differ in reactivity characteristics.

135. The process of claim 128, wherein the coupling compound is a compact molecule and contains three α,α-disubstituted olefin groups and wherein the molar ratio is controlled to form a star copolymer with up to six arms.

136. The process of claim 118, wherein the coupling compound contains two α,α-disubstituted olefin groups of different reactivities and the first polymer and second polymer each have two radically transferable atoms or groups resulting in one of an

extended chain or coupled polymer with an α,α-disubstituted olefin group within the chain.

137. The process of claim 126, wherein the coupling compound contains three α,α-disubstituted olefin groups and the molar ratio of the total moles of the first polymer and the second polymer to the moles coupling compound is controlled to form a star polymer with up to six arms.

138. The process according to 128, wherein the molar ration is 1:0.167.

139. The process of claim 118, wherein the coupling compound comprises a third polymer.

140. A star copolymer, comprising segments of free radically polymerizable monomers wherein two or more arms have a different composition from the other arms.

141. A star copolymer produced by the process of claim 128, wherein the first polymer and the second polymer are different.

142. The star copolymer of claim 141, wherein the first polymer differs from the second polymer in at least one of molecular weight or composition.

143. A graft copolymer with a backbone polymer with incorporated coupling compounds and a grafted polymer produced by process of claim 118.

144. The graft copolymer of claim 143, wherein the backbone polymer is produced by an addition or condensation polymerization process.

145. The graft copolymer of claim 143, wherein the backbone polymer is a polyolefin.

146. The graft copolymer of claim 143, wherein the backbone polymer comprises blocks of at least one of polystyrene, polyethylene, polypropylene, polyisobutylene, polybutadiene or polyisoprene.

147. An α-substituted olefin, comprising an exo-double bond, suitable for use as a macromonomer, in which the α-substituant is a free radically (co)polymerized oligo/polymer with a molecular weight greater than 250 possessing a known group at the other terminus of the polymer.

148. An α,β-disubstituted olefin comprising two substituants, wherein each substituant is a free radically (co)polymerized oligo/polymer with a molecular weight greater than 250.

149. A macromonomer comprising:

a functional group containing a terminal exo-olefin double bond derived from free radically (co)polymerizable monomers;

a stereochemistry and tacticity of a material formed by a free radical polymerization process; and

a symmetrical single peak molecular weight distribution less than 1.5.

150. The macromonomer of claim 149, wherein the functionality is greater than 90 mole %.

151. A controlled polymerization process, comprising:

adding a core forming compound to an active atom transfer radical polymerization process; and

forming a multi-arm star copolymer wherein polymers react with the core forming compound to form the star compound.

152. The process of claim 151, further comprising:

adding a plurality of initiators, wherein each initiator includes:

a radically transferable atom or group; and

optionally, a functional group.

153. The process of claim 152, wherein the core forming compound is a divinyl compound.

154. The process of claim 153, wherein the multi-arm star polymer includes a single well defined core.

155. The process of claim 153, wherein the multi-arm star polymer includes a core having core compound to core compound coupling.

156. The process of claim 153, wherein the multi-arm star polymer includes a network of coupled core compounds.

157. The process of claim 153, wherein the resulting multi-arm star polymer is a one of a gel or crosslinked system.

158. The process of claim 153, wherein the divinyl compound is one of a divinyl aryl compound, a di-acrylate or a di-methacrylate.

159. A telefunctional multi-arm star copolymer comprising:

a core comprising core unit to core unit coupling;

a plurality of arms synthesized from radically polymerizable monomers attached to at least one of the core units; and

a known level of functional groups on the termini of each polymer chain.

160. A crosslinked or gel-like telefunctional multi-arm star copolymer comprising:

at least two core units;

a plurality of arms synthesized from radically polymerizable monomers attached to at least one of a core unit and another arm forming a matrix; and

a known level of functional groups with in the matrix.

161. A telefunctional network copolymer produced by the process of claim 141, wherein:

the average number of radically transferable atoms or groups per first polymer is greater than one; and

the core compound is a divinyl compound.

162. A telefunctional multi-arm star copolymer wherein the arms of the copolymer are composed of different copolymers displaying differing properties.

163. A polymerization or telomerization process for preparation of polyvinyl acetate with a predetermined molecular weight range comprising:

polymerizing a vinyl acetate monomer in the presence of a system comprising:

an initiator having a radically transferable atom or group, wherein in the initiator is also capable of acting as a chain transfer agent; and

a transition metal complex which participates in a redox reaction with at least one atom or group of the initiator having a radically transferable atom or group, the transition metal complex comprising:

transition metal;

a ligand coordinated with the transition metal to form a partially soluble transition metal complex.

164. The process of claim 163, further comprising:

forming polyvinyl acetate having a radically transferable atom at one polymer end; and

optionally, isolating the polyvinyl acetate.

165. The process of claim 163, wherein the chain transfer rate constant of the initiator in the system is about one and remains substantially constant throughout the polymerization.

166. The process of claim 163, wherein the initiator is at least one of carbon tetrahalide or an alkyltrihalide.

167. The process of claim 166, wherein the halide is a bromide or a chloride.

168. The process of claim 163, wherein the transition metal is iron.

169. The process of claim 168, wherein the ligand is a linear amine.

170. The process of claim 169, wherein the ligand is a tetramine.

171. The process of claim 163, wherein the transition metal complex further comprises:

a counterion which is not a radically transferable atom or group.

172. The process of claim 171, wherein the counterion is an acetate.

173. The process of claim 163, further comprises:

controlling the polymerization by adding a predetermined amount of initiator based on the amount of vinyl acetate to be polymerized;

forming polyvinyl acetate of a predetermined average molecular weight.

174. The process of claim 163, wherein the polymerization is a telomerization and further comprising:

forming a polyvinyl acetate telomer.

175. The process of claim 174, further comprising:

controlling the telomerization by adding a predetermined amount of initiator based on the amount of vinyl acetate to be telomerized, wherein the initiator is one of carbon tetrahalide or an alkyltrihalide group on a molecule having at least one alkyltrihalide group; and

forming the polyvinyl acetate telomer at a predetermined average molecular weight.

176. The process of claim 175, wherein the polyvinyl acetate has a terminal radically transferable atom or group.

177. The process of claim 174, wherein the molecular weight of the polyvinyl acetate telomer is less than 1,000,000.

178. The process of claim 174, wherein the molecular weight of the polyvinyl acetate telomer is between 1,000 and 100,000.

179. The process of claim 175, further comprising:

converting the vinyl acetate telomer into a alkoxyamine macroinitiator.

180. A process for the preparation of vinyl acetate block copolymers comprising:

polymerizing free radically (co)polymerizable monomer in the presence of a system initially comprising:

a polyvinyl acetate based macroinitiator having a radically transferable atom or group; and

a catalyst which participates in a reversible cycle with at lease one of the macroinitiator and a compound having a radically transferable atom or group.

181. The process of claim 180, further comprising:

first preparing a polyvinyl acetate based macoinitiator comprising:

polymerizing a vinyl acetate monomer in the presence of a second system comprising:

an second initiator having a second radically transferable atom or group, wherein the second initiator is also capable of acting as a chain transfer agent; and

a partially soluble transition metal catalyst which participates in a redox cycle with the second initiator and in a reversible cycle with the polyvinyl acetate macroinitiator or a compound having a radically transferable atom or group, the transition metal catalyst comprising:

a transition metal;

a ligand coordinated with the transition metal to form the transition metal complex.

182. The process of claim 181, wherein the second initiator includes a alkyltrihalide group and the polyvinyl acetate based macroinitiator contains two telechelic groups having a radically transferable atom or group.

183. The process of claim 182, wherein the alkyltrihalide is an alkyldichlorobromo-group and the telechelic groups have terminal bromo groups.

184. The process of claim 181, wherein preparing a polyvinyl acetate based macroinitiator further comprises:

isolating the polyvinyl acetate based macroinitiator.

185. The process of claim 181, wherein the catalyst is the transition metal complex.

186. A process for the preparation of block copolymers, comprising:

preparing a radically (co)polymerizable polymer comprising:

polymerizing a first radically (co)polymerizable monomer in the presence of a first system comprising:

an initiator having a radically transferable atom or group, wherein the initiator is also capable of acting as a chain transfer agent; and

a transition metal complex which participates in a reversible cycle with at least one of the initiator and a compound having a radically transferable atom or group;

adding and polymerizing a second free radically (co)polymerizable monomer in the presence of a second system initially comprising:

the radically (co)polymerizable polymer having a radically transferable atom or group, wherein the radically (co)polymerizable polymer acts as the initiator; and

the transition metal complex, wherein the transition metal complex is at least partially soluble in the second system and participates in a reversible cycle with at least one of the radically (co)polymerizable polymer and a compound having a radically transferable atom or group; and

optionally, isolating the block copolymer.

187. The process of claim 186, wherein the second system further comprises:

the first radically copolymerizable monomer.

188. A block copolymer, comprising:

a first block synthesized from vinyl acetate monomers; and

a second block of free radically copolymerizable monomers attached to the first block.

189. A process for the preparation of block copolymers comprising:

polymerizing a first (co)polymer block by a first reaction mechanism catalyzed by a transition metal; and

polymerizing a second (co)polymer block by a second reaction mechanism catalyzed by the transition metal, wherein the first reaction mechanism is different than the second reaction mechanism.

190. A block copolymer, comprising:

a first block synthesized from vinyl acetate monomers; and

a second block synthesized from free radically copolymerizable monomers and, optionally, having functional end groups.

191. The process of preparing a block copolymer, comprising the steps of:

providing a block copolymer comprising:

a first block synthesized from vinyl acetate monomers; and

a second block of free radically copolymerizable monomers having functional end groups;

converting the functional end group into a different group.

192. An ABA block copolymer having functional end groups, comprising:

two A blocks synthesized from vinyl acetate monomers; and

a B block synthesized from free radically copolymerizable monomers.

193. The process of preparing a ABA block copolymer, comprising the steps of:

providing an ABA block copolymer having functional groups comprising:

two A blocks synthesized from vinyl acetate monomers; and

a B block synthesized from free radically copolymerizable monomers; and

converting the functional end group into a different group.

194. An AB star copolymer, comprising:

an A block synthesized from vinyl acetate monomers; and

a B block synthesized from free radically copolymerizable monomers.

195. A block copolymer comprising:

a first block synthesized from vinyl acetate monomers; and

a second block synthesized from (meth)acrylate monomers.

196. A polymerization process for the preparation of homopolymers and block polymers with (meth)acrylamide monomers comprising:

copolymerizing a (meth)acrymide monomer in the presence of a system initially comprising:

a initiator having a radically transferable atom or group; and

a transition metal complex which participates in a reversible redox cycle with at lease one of the macroinitiator and a compound having a radically transferable atom or group, wherein the transition metal complex allows addition of several monomer units during each reversible redox cycle;

forming a polymer.

197. The process of claim 196, wherein the initiator is a macroinitiator.

198. A (meth)acrylate-block-(meth)acrylamide copolymer produced by the polymerization process of claim 196.

199. A controlled suspension or emulsion polymerization process comprising:

polymerizing free radically (co)polymerizable monomers in the presence of a system initially comprising:

a suspending medium;

a surfactant;

an initiator having a radically transferable atom or group; and

a transition metal complex which participates in a reversible redox cycle with at least one of the initiator and a compound having a radically transferable atom or group, wherein the redox conjugate of the catalyst transition metal is added to the suspending medium.

200. The process of claim 199, wherein the hydrophobicity and hydrophylicity of the transition metal complex is controlled by the choice of one of the ligands or the substituents on the ligands.

201. The process of claim 200, further comprising:

adding a second free radically (co)polymerizable monomer; and

optionally, adding at least one of the transition metal complex , the transition metal compound, the transition metal redox conjugate, a counterion comprising a second radically transferable atom or group, and a ligand.

202. The process of claim 199, wherein the transition metal complex comprises a picolyl amine.

203. The process of claim 199, wherein the polymerization is initiated by the decomposition of a standard radical initiator.

204. An emulsion controlled radical polymerization process, comprising:

providing a suspension medium;

adding a standard free radical initiator, initiating the polymerization by decomposition of the standard free radical initiator, in the presence of radically (co)polymerizable monomers

adding a transition metal compound in a higher oxidation state comprising a radically transferable atom or group, wherein the radically transferable group transfers to the residue of the standard free radical initiator to form a second initiator; and

adding a third initiator having a radically transferable atom or group.

205. The process of claim 204, further comprising:

forming an emulsion in the suspending medium, wherein the particle size of the emulsion is controlled by the decomposition of the standard free radical initiator and the polymerization process is controlled by the second and the third initiators.

206. A controlled radical polymerization process, comprising:

contacting an initiator attached to a solid surface to a solution comprising:

a plurality of free radically polymerizable monomers; and

a persistent free radical formed in the controlled radical polymerization.

207. The process of claim 206, further comprising:

a free radically (co)polymerizable monomer; and

a persistent free radical or deactivator.

208. The process of claim 207, further comprising a transition metal compound as the persistent free radical or deactivator.

209. The process of claim 207, wherein the persistent free radical is greater than 1% of the solution.

210. The process of claim 207, wherein the persistent free radical is greater than 3% of the solution.

211. The process of claim 207, wherein the persistent free radical is greater than 1% of the system and the monomer.

212. The process of claim 207, wherein the persistent free radical is greater than 3% of the system and the monomer.

213. The process of claim 207, wherein the persistent free radical is the redox conjugate of a transition metal catalyst.

214. The process of claim 207, wherein the persistent free radical is the stable free radical.

215. The process of claim 207, wherein the solid surface is one of an inorganic surface or on inorganic particle.

216. The process of claim 207, wherein the initiator comprises a functional group attached to the solid surface through a non-aromatic group.

217. A controlled polymerization process, comprising:

a predetermined solvent concentration, wherein the solvent concentration is predetermined to control the concentration of the persistent free radical or deactivator

218. A controlled polymerization process, comprising:

an unsaturated monomer having an attached polyhedral oligomeric silsesquioxane group.

219. The process of claim 218, wherein the unsaturated monomer is a vinyl aromatic.

220. The process of claim 218, wherein the unsaturated monomer is a (meth)acrylate.

221. The process of claim 218, further comprising:

forming a polymer.

222. The process of claim 221, wherein the polymer is a homopolymer, a copolymer, a block copolymer, or a star block polymer.

223. A homogeneous reverse atom transfer polymerization, comprising:

polymerizing free radically (co)polymerizable monomers in the presence of a system initially comprising:

a first standard radical initiator, wherein the first standard radical initiator is decomposed;

a transition metal complex in a lower oxidation state and having a radically transferable atom or group, wherein the radically transferable atom or group is transferred to the residue of the first standard radical initiator forming a second initiator, wherein the transition metal complex participates is reversible cycle with the second initiator and a compound having a radically transferable atom or group; and

forming a polymer.

224. A multifunctional star (co)polymer, comprising:

a core compound;

a plurality of polymer arms synthesized from free radically copolymerizable monomers having a functional end and an attached end, wherein the attached end is attached to the core compound;

a functional group attached to the functional end of the polymer arms.

225. The multifunctional star (co)polymer of claim 224, wherein in the polymer arms are of controlled molecular weights and wherein the functional groups present on the outer layer of the star (co)polymer have been added by an atom transfer addition reaction.

226. The polymer of claim 224, wherein the free radically copolymerizable monomers include (meth)acrylates and (meth)acrylic acids.

227. The multifunctional star (co)polymer, wherein the functional group is selected from hydroxy, epoxy, amino, cyano, halide. wherein the functional group us present on the functional end of the polymer arms.

228. A controlled polymerization process for the preparation of block copolymers, comprising:

polymerizing a plurality of first monomers into a polymer chain;

polymerizing a second monomer into the polymer chain, wherein a second monomer is polymerized while some of the first monomer remains unpolymerized.

229. The process of claim 228, wherein the first and second monomers are free radically polymerizable monomers, and polymerizing the first and second monomers comprises a persistent free radical, a deactivator, or a redox conjugate of the catalyst.

230. The process of claim 229, wherein the system further comprises a solvent.

231. The process of claim 228, wherein adding and polymerizing a second free radically (co)polymerizable monomer is conducted after 75% of the first monomer is polymerized.

232. A block copolymer produced by the process of claim 231.

233. The process of claim 228, wherein adding and polymerizing a second free radically (co)polymerizable monomer is conducted after 50% of the first monomer is polymerized.

234. A block copolymer produced by the process of claim 233.

235. A block copolymer, comprising:

a first block synthesized from a first monomer;

a second block synthesized from a second monomer; and

a third block synthesized from both the first and second monomer.

236. The block copolymer of claim 235, wherein the third block comprises a gradient of the concentration of first monomers from the first block to the second block.

237. The block copolymer of claim 236, wherein the third block comprises a gradient of the concentration of first monomers from the second block to the first block.

238. A process for the preparation of hybrid block copolymers comprising:

polymerizing free radically (co)polymerizable inorganic monomer in the presence of a system initially comprising:

a organic based macroinitiator having a radically transferable atom or group; and

a catalyst which participates in a reversible cycle with at lease one of the macroinitiator and a compound having a radically transferable atom or group.

239. The process of claim 238, further comprising:

converting an organic polymer into the macroinitiator by modifying an end group.

240. The process of claim 239, wherein modifying an end group comprises converting a first end group into a second end group.

241. The process of claim 238, wherein the macroinitiator is a phosphoramine.

242. A process for preparation of graft polymers, comprising:

(co)polymerizing a macromonomer in the presence of a macroinitiator compatible with the macromonomer.

243. A process of claim 242, wherein (co)polymerizing comprises a radical polymerization process and the macromonomer has a terminal olefinic bond.

244. The process of claim 243, wherein the macromonomer includes a terminal α, α-disubstituted olefin group.

245. The process of claim 243, wherein the macromonomer includes a terminal α-methylstyryl or isopropyl benzyl group.

246. The process of claim 242, further comprising:

a catalyst which participates in a reversible cycle with the macroinitiator; wherein the macroinitiator is a macroinitiator having a radically transferable atom or group.

247. A controlled polymerization process, comprising:

polymerizing free radically (co)polymerizable monomers in the presence of a system initially comprising:

an initiator having a radically transferable atom or group; and

a transition metal complex comprising:

a transition metal catalyst which participates in a reversible cycle with at least one of the initiator and a compound having a radically transferable atom or group, wherein transition metal complex catalyst comprising:

a ligand coordinated with the transition metal and wherein the ligand is attached to a support.

forming a (co)polymer.

248. The process of claim 247, further comprising:

adding a redox conjugate of the transition metal to the reaction system.

249. The process of claim 248, wherein the redox conjugate of the transition metal is added to the reaction system prior to the initiation of the polymerization.

250. The process of claim 247, wherein the transition metal is in both the higher and the lower oxidation states.

251. The process of claim 250, wherein the redox conjugate state of the transition metal is present at 5 weight % of the total transition metal.

252. The process of claim 247, wherein the ligand comprises a linear amine.

253. The process of claim 252, wherein the linear amine is a linear tetramine.

254. The process of claim 247, wherein the support is a polymeric support.

255. A block copolymer, comprising:

at least two blocks synthesized from free radically (co)polymerizable monomers wherein one of more blocks comprise a copolymer of the monomer(s) in the other block(s) with a second monomer.

256. A block copolymer, comprising:

at least two monomer blocks synthesized by at least one of a first free radically (co)polymerizable monomer and a second free radically (co)polymerizable monomer, wherein at least one block comprises a tapered copolymer.

257. An AB block copolymer, comprising:

a first block synthesized from a first free radically polymerizable monomer;

a second block synthesized from a second monomer and the first monomer, wherein the concentration of the first monomer in the second block increases the greater the distance from the first block along the polymer chain.

258. The block polymer of claim 257, wherein the first monomer and the second (co)monomer differ in phylicities.

259. A controlled polymerization process, comprising:

polymerizing free radically (co)polymerizable monomers in the presence of a system at a polymerization temperature, the system initially comprising:

an initiator having a radically transferable atom or group;

a transition metal complex which participates in a reversible cycle with at least one of the initiator and a compound having a radically transferable atom or group; and

a solvent;

forming a polymer, wherein the polymer is soluble in the solvent at the polymerization temperature;

altering at least one of the temperature, the polarity or the pressure of the system to a precipitation temperature wherein the polymer is not soluble in the solvent.

260. The process of claim 259, wherein the transition metal complex is soluble in the solvent at the polymerization temperature and the precipitation temperature.

261. The process of claim 260, further comprising:

separating the polymer from the system.

262. The process of claim 261, wherein separating the polymer comprises filtering the polymer from the system.

263. The process of claim 259, wherein the solvent is a polar solvent.

264. The process of claim 259, wherein the solvent is a non-polar solvent.

265. The process of claim 259, wherein the transition metal complex comprises a ligand.

266. A controlled polymerization process, comprising:

polymerizing a first free radically (co)polymerizable monomer and a radically copolymerizable monomer in the presence of a system initially comprising:

an initiator having a radically transferable atom or group; and

a catalyst which participates in a reversible cycle with at least one of the initiator and a compound having a radically transferable atom or group.

267. The process of claim 266, wherein the second free radically copolymerizable monomer comprises a second functional group.

268. The process of claim 267, wherein the second functional group comprises a polar substituent.

269. The process of claim 268, wherein the polar substituent is a carboxylic acid group.

270. A homo-telechelic copolymer, comprising:

a polymer synthesized from free radically copolymerizable monomers having a first terminal end and a second terminal end;

a first functional group attached to said first terminal end;

a second functional group attached to said second terminal end, wherein the said second functional group has a different reactivity than said first functional group.

271. The controlled polymerization process for the production of telefunctional multi-arm star copolymers, comprising:

polymerizing a free radically (co)polymerizable monomer in the presence of a system comprising:

a telefunctional multi-armed star initiator synthesized from free radically copolymerizable monomers, a first initiator with one radically transferable atom or group, and a divinyl compound.

272. The process of claim 271, wherein the first initiator further comprises a second functional group.

273. The controlled polymerization process, comprising:

polymerizing a free radically (co)polymerizable monomer in the presence of a system comprising:

a transition metal catalyst comprising a ligand.

274. The process of claim 273, wherein the ligand and the substituents are chosen to control the hydrophylicity and the hydrophobicity of the catalyst.

275. The process of claim 273, wherein the ligand and the substituents are chosen to partition sufficient concentration of the redox conjugate of the catalyst into the system to control the polymerization.

276. The process of claim 273, wherein the structure of the ligand is chosen to control the redox potential of the catalyst complex in the polymerization system.

277. A graft copolymer, comprising:

a polyolefin backbone polymer; and

a poly(meth)acrylate grafted on the backbone polymer.

278. The graft copolymer of claim 277, wherein the poly(meth)acrylate comprises (meth)acrylic acid units.

279. A controlled polymerization process, comprising:

a free radically polymerizable monomer in the presence of a system comprising:

an initiator, wherein the initiator comprises a radically transferable atom or group attached to the particle surface through a non-aromatic linking group.

280. A process for the preparation of a composite structure, comprising:

polymerizing one or more free radically polymerizable (co)monomers in the presence of an initiation system comprising:

a functional silica particle initiator comprising:

a silica particle; and

a functional group containing a radically transferable atom;

a catalyst comprising a transition metal complex which participates is a reversible cycle with at least one of the initiator and a compound having a radically transferable atom or group.

281. The process of claim 280, wherein the silica particle is a monodisperse particle.

282. A process for the preparation of a composite structure, comprising:

polymerizing one or more free radically polymerizable (co)monomers in the presence of an initiation system comprising:

a functionalized nanotube initiator comprising:

a functional group containing a radically transferable atom;

a catalyst comprising a transition metal complex which participates is a reversible cycle with at least one of the initiator and a compound having a radically transferable atom or group.

283. A self reinforced nanocomposite comprising:

a matrix synthesized from free radically polymerizable monomers.

284. A process for removal of a catalyst from a polymerization system, comprising:

adding a compound to a polymerization system comprising:

a catalyst; and

a polymer;

wherein the compound causes precipitation of the catalyst from the polymerization system by interaction with the catalyst;

filtering the reaction system to remove the catalyst.

285. A process for removal of a catalyst from a polymerization system, comprising:

altering at least one parameter of a polymerization system comprising:

a catalyst; and

a polymer;

wherein the parameters are selected from a group consisting of polarity of the system, temperature and pressure which causes precipitation of the catalyst from the polymerization system;

filtering the reaction system to remove the catalyst.